Tandem Hybrid Solar Energy System

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Objectives

Our goal is to demonstrate a 20% efficient generation II photoelectrochemical system for hydrogen and solar electricity generation. As our system is primarily limited by the dye sensitized solar cell performance, we need to make at least 8% efficient dye cells with areas of at least 0.75 cm^2 to attain the 20% system goal. Although there are several possible paths for improvement of the dye-cell, our primary approach has been to increase the dye cell performance by increasing the red absorbance of the commonly used N719 dye through the use of photonic crystal layers. Other goals of higher system level efficiency may be obtained by redesigning the system, fabricating higher performing counter-electrodes, attaining better charge transport through the nano-titania, and improving the performance of the silicon cell component.

Technical Barriers

System modeling shows that the primary factors limiting the efficiency of this tandem system are the low inherent solar efficiency of dye-sensitized solar cells (DSSCs) and the loss of active area of the DSSC necessitated by sealing and wiring. Our 20% improvement in dye absorbance and incident-photon-conversion efficiency of photonic crystal enhanced nano-titania dye cells to routine ~8.5% efficient cells has been limited by optical coupling of the photonic crystal layer to the nano-titania. At the same time, this increased performance in 0.25 cm^2 dye cells must be scaled to work with our system designs. If this can be achieved, it would improve our present 14.5% system to 17.5% under similar testing conditions. With increased scaling come higher electrode losses. Thus we are also studying charge transfer characteristics of higher performing counter electrode materials. Finally, the most important technical barrier to system performance is electron transport through the titania films which is being addressed through new processing methods to make crystalline titania rods and sheets on the anode electrode surface.

Abstract

Having established a baseline outdoor efficiency of 14.5% for our tandem dye sensitized solar cell-silicon cell hybrid concentrator system, our work has focused on understanding and improving factors limiting this system. We have identified factors, each of which can improve the system level efficiency by at least 1%, and are working to improve many of these. Although some of these factors are engineering- and design-related, such as improved silicon photovoltaic

efficiency and improved optical design, the primary limiting factors - dye performance, electron transport in titania, resistive losses in the dye cell electrodes, loss of redox couple, iodine/iodide redox couple - are direct or indirectly related to the performance of the dye sensitized solar cell.

Progress Report

Limits to the Efficiency of Dye Based Solar Cells. The DSSC has long been promised as a low cost alternative to silicon photovoltaics.[1,2] Despite intense interest and study, it is well known that one can reproducibly make 6-7% efficient cells. However, only a few groups have reported laboratory cells in excess of 10%.[3,4] For the current nanoparticle-based dye cell, a simple way of improving efficiency is to extend the range of dye absorbance further into the red part of the solar spectrum. For our tandem cell system this increased absorbance could yield a 10% gain in dye cell performance because the standard N-719 dye is absorbing only ~60% of the photon flux at 620 nm as shown in Figure 1. Figure 1 also shows our tandem hybrid system is utilizing < ~85% of the flux between the wavelengths of 580-720 nm. Thus by extending the range of absorbance of the dye, our system level efficiency should increase, assuming equivalent electron transport rates. The method we are pursuing to improve the photoresponse of the N-719 dye (as well as more recently developed black absorber dyes) is to create standing waves of light through the use of a photonic crystal.
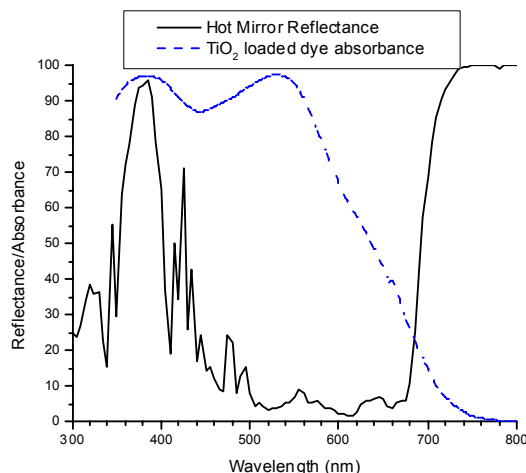

Figure 1. Hot mirror coated FTO reflectance and absorbance spectrum of a 14 μm N719 dye coated nanoparticulate film as a function of wavelength, showing poor spectral utilization between 600-700 nm.

Improved Photoresponse of a Dye Sensitized Solar Cell Through Photonic Crystals. In our previous work, we showed that coupling of TiO_2 inverse opals to nano-TiO_2 films improved the red response of the dye cell substantially through a "standing wave" effect, in which light scattered by the photonic crystal is localized in the dye-sensitized nano-TiO_2 layer. In Subsequent modeling studies have shown that intimate coupling between these layers is needed to realize this effect. A practical drawback of these cells was that the nano-TiO2 layer could be deposited on top of the inverse opal layer on the anode, but the order of the layers could not be inverted. This meant that the cells were illuminated from the cathode side, i.e., through the electrolyte, resulting in inevitable losses in the blue part of the spectrum. Recently, we have developed a polymer templating method that has allowed us to grow the inverse opal on top of the nano-TiO_2 films, and thus illuminate from the anode side. Two interesting findings have emerged from this work. First, careful studies with many cells, using optimized layer thicknesses and identical quantities of adsorbed dyes, show that the scattering layer increases the average AM 1.5 efficiency of 0.25 cm^2 cells from 6.5 to 8.3%. Second, we find that this method still leaves sufficient gaps between the two layers that we have not achieved the full standing wave coupling effect. We are thus optimistic that further refinement of the method will lead to additional improvements in light utilization.

Growth of Oriented Nanorods on FTO. An important factor in dye cell performance is theelectron transport rate through the titania via trap-to-trap hopping.[5,6] It is thought that by growing

vertically-oriented single crystal anatase and eliminating grain boundaries, which contain significant number of defect sites, electron transport would be enhanced. Recently, it has been shown that well aligned vertical columns of sodium titanates may be grown by reacting Ti-Al-V foil in 1 M aqueous NaOH at temperatures above 180 °C.[7] These sodium titanates may then be transformed to hydrogen titanates through an ion exchange process, and then to anatase through dehydration at elevated temperatures. This process will not work on FTO as it is not stable in aqueous sodium hydroxide at elevated temperatures, and there will still be substantial resistive losses due to heating FTO to elevated temperatures. However, other reports show that it is possible to grow vertically aligned pillars of anatase on FTO by exposing titania powder to aqueous 5 M NaOH at room temperature.[8] The overall efficiency of the cell was < 1% due to low nucleation density and surface area of the titania and the cell still required annealing at 450 °C. It remains to be seen whether these samples are polycrystalline or single crystal and whether charge transport is any faster than in nano-titania films of equivalent thickness. We have verified the growth of sodium titanate nanowires on titanium foil, are currently exploring the low temperature sodium hydroxide treatment of titania powder, as well as exploring other materials systems.

We have also grown vertically aligned titania nanowires on FTO by a new template-free techniques in which titanium trichloride is hydrothermally treated wth aqueous NaCl at 200 °C. We have also grown vertically aligned titanium glycolate rods on FTO. What is intriguing about the glycolate rods is they may be converted to anatase through hydrolysis but they are already effectively ligand-capped 1-D titania nanowires, and the individual nanowires can be grown 10's of micrometers long. This is a very interesting system in which to study quasi-1D transport.

Improved Silicon Cell Performance and Overall System Level Performance. The silicon cell that had been used in our previous outdoor experiments has a 1-sun efficiency of ~16%. Using only the radiation reflected by the hot mirror improves the efficiency to 18.1%. This very modest increase in efficiency utilizing primarily the infrared radiation suggests that the silicon cell is limiting the overall system performance by not absorbing all of the incident infrared photons. We are now collaborating with Prof. Martin Green to use higher performing silicon cells in our tandem hybrid system. These improved silicon cells have a measured outdoor global efficiency of 18-19% and a 'hot mirror' efficiency of 23%. Under equivalent testing conditions, system modeling shows that the module efficiency should increase by ~ 2.5% with these cells.

Improved System Level Design. An alternate tandem hybrid concentrator design is the cold mirror arrangement shown in Fig. 2. In this design, sunlight irradiates the system from the left and a low-cost dielectric cold mirror on the front surface of the triangular prisms reflects only visible light to the DSSCs, which are stacked perpendicular to the prism bases as shown for one unit cell in the left pane. The DSSCs would be packaged by their platinized electrodes and stacked back-to-back, or would be transparent DSSCs (as demonstrated by Solaronix), collecting diffuse light from both sides. The right image shows the path of infrared rays in the system and the Si cell locations. A significant advantage of the cold mirror system is the 'wasted space' border area required for sealing the cells in the hot mirror geometry can extend below the prism bases and the active area of the dye cell can be matched to the height of the prisms. As a result, for 8% efficient dye cells, this system should achieve module efficiencies 2.5% higher than
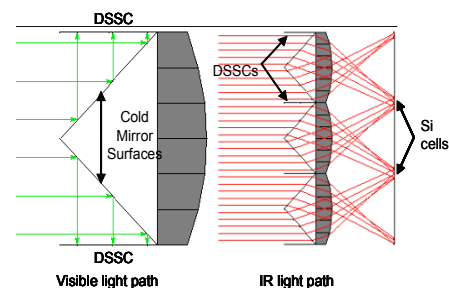

Figure 2. Ray tracing optical modeling results for a cold mirror-based hybrid DSSC-Si module. The visible light response for one unit cell is shown in the left panel and the right panel shows the IR response and Si cell locations.

the hot mirror concentrator design, because all of the visible rays are directed to the active area of the DSSC. Because of the anticipated increased efficiency, the wider tolerances offered by refractive optics in terms of testing in sunlight, and the difficulties we have encountered in sealing small DSSCs for the hot mirror concentrator module, we now are exploring this configuration.

Future Directions
1. Photonic crystal enhanced dye sensitized solar cell – improve the coupling between the photonic crystal and the nano-particulate dye sensitized solar cell to achieve enhanced red absorption, as has been observed in the inverted photonic crystal nano-TiO_2 bilayer structure.
2. Implement new system design and improved silicon cells to gain several % in efficiency.
3. Fabricate and evaluate improved counter electrode materials by impedance spectroscopy and measure resistive losses for improved large-area DSSC performance.
4. Continue developing single crystal nanowires of titania on FTO and measure electron transport properties.
5. Perform electronic structure calculations to evaluate the band structure of titanium glycolate nanowires and measure the transport properties of electrons in titanium glycolate crystals.

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